

**ANTHRAQUINONE:1, 8 ALIPHATIC THIO-
ETHER-SULPHONIC ACIDS AND
DI-THIO-ETHERS.**

A DISSERTATION

**SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY.**

**BY
GEORGE EDGAR MILLER**

June 1920.

**ANTHRAQUINONE:1, 8 ALIPHATIC THIO-
ETHER-SULPHONIC ACIDS AND
DI-THIO-ETHERS.**

A DISSERTATION

**SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY.**



**BY
GEORGE EDGAR MILLER**

June 1920.



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41546703_0088

CONTENTS.

Acknowledgment	4
Introduction	5
Historical	6
Properties	8
Experimental	9
Procedure	9
Plan	12
Anthraquinone-1-Thio-Ether-8-Sulfonic Acids	13
Biography	29

ACKNOWLEDGMENT.

The work described in the following pages was carried out at the suggestion and under the supervision of Dr. E. Emmet Reid. The writer wishes to take this opportunity to thank him for his help and interest in this work. He also wishes to thank Drs. Remsen, Frazer, Patrick, Lovelace, Lloyd and Swartz for instruction received from them during his course as a student at Johns Hopkins University.

The writer also feels under obligations to Drs. Thornton, and Millikan for helpful suggestions which they made.

ANTHRAQUINONE:1, 8 ALIPHATIC THIO- ETHER-SULFONIC ACIDS AND DI-THIO-ETHERS.

INTRODUCTION.

In the hope of obtaining derivatives of anthraquinone-sulfonic acids which would have suitable melting points for their identification, the problem of replacing sulfonic acid groups was undertaken. It was known that sulfonic acid groups of anthraquinone-sulphonic-acids could be replaced by methoxy¹ or phenoxy groups² and that the resulting compounds, $C_{14}H_7O_2.OCH_3$ and $C_{14}H_7O_2.OC_6H_5$ are crystalline and have definite though rather high melting points.

Hence it was thought that a compound of the formula $C_{14}H_7O_2.SR$ would be of service. Normal butyl mercaptan was used as being readily available, and it was thought probable that the compound would have a low melting point, since sulfur compounds usually melt lower than the corresponding oxygen compounds and since butyl derivatives are apt to melt considerably lower than methyl and much lower than phenyl derivatives. The desired reaction was found to take place readily, although not quantitatively when the sulfonic acid group is in the alpha position and the resulting compounds were found to have convenient melting points suitable for the identification of anthraquinone alpha sulphonic acid and anthraquinone 1,5 and 1,8 disulphonic acids.

The ease with which the reaction takes place and the interesting character of the compounds obtained led to a study of derivatives of other mercaptans in combination with 1,8 disulfonic acid.

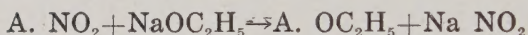
1 D. R. P. 156762.

2 D. R. P. 158531.

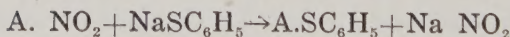
HISTORICAL.

Anthraquinone aliphatic thio-ether-sulfonic acids and di thio-ethers may be prepared by the action of aliphatic mercaptans on anthraquinone sulfonic acids in alkaline solution.³ In this way Bayer and Company prepared anthraquinone 1, ethyl-thio-ether, 5 sodium-sulphonate and 1,5 di-ethyl-thio-ether.

Gattermann⁴ has shown that the nitro group in nitro anthraquinone is replaced by the alkoxy group when treated with sodium alcoholate, thus:



Representing the anthraquinone residue by A. He attempted to carry out the analogous reaction using alkaline mercaptan in order to obtain anthraquinone-thio-ether. This reaction, however, resulted in the reduction of the nitro group to the amino group. On the other hand he found that treatment with alkaline aromatic mercaptans readily caused a quantitative replacement of the nitro group with the formation of aromatic thio-ethers.



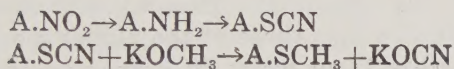
Gattermann⁵ has also prepared anthraquinone ali-

³ D. R. P. 224589.

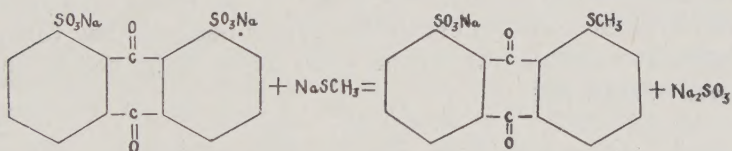
⁴ D. R. P. 75054.

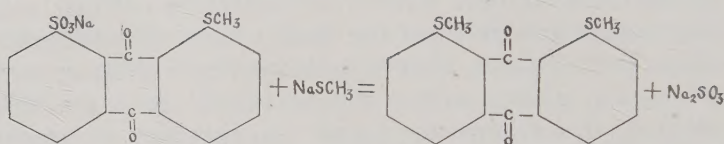
⁵ Loc. cit., and Liebig's Annalen, 303, 138-139, 179-180 (1912).

phatic thio-ethers and thio-ether-sulfonic-acids indirectly by diazotizing amino-anthraquinones or amino anthraquinone-sulfonic acids in concentrated sulfuric acid. Subsequent treatment of the diazo compound with potassium thio cyanate yielded anthraquinone thio cyanate which on boiling with alcoholic potash gave the thio-ether or thio ethersulfonic-acid. In this way he prepared anthraquinone alpha ethyl-thio-ether; anthraquinone methyl-thio-ether 5 potassium sulfonate; and anthraquinone methyl-thio-ether 8 potassium sulfonate, thus:



In the present investigation it is shown that anthraquinone 1,8 di sodium sulfonate when heated with aliphatic mercaptans in alkaline solutions react readily to form thio-ether-sulfonic-acids and di-thio-ethers, the sulfonic acid groups being replaced in turn according to the following reactions:—





PROPERTIES.

The anthraquinone thio-ether-sodium-sulfonates are soluble in water, the derivatives of the lower mercaptans being more soluble than those of the higher mercaptans. They crystallize from water in orange to orange red needles containing one molecule of water of hydration with the exception of the propyl derivative which contains one-half molecule of water. Other salts of these acids are highly colored ranging from light yellow through shades of orange to red, and are in general well crystallized.

Anthraquinone di-thio ethers are insoluble in water, slightly soluble in alcohol and very soluble in benzene. In this case the derivatives of the higher mercaptans are markedly more soluble than those of the lower members of the series. When crystallized from benzene they form lustrous crystals varying in color from light yellow to deep orange red.

EXPERIMENTAL.

MATERIALS.

The anthraquinone 1,8 di-sodium-sulfonate was obtained through the courtesy of E. I. du Pont de Nemours & Company.

The methyl mercaptan was generated by dropping dimethyl sulfate into warm sodium hydrosulfide, which was prepared by warming $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ to about 90°C , and saturating with hydrogen sulfide.

The ethyl mercaptan was prepared in a similar manner using sodium ethyl sulfate.

The propyl, butyl and iso amyl mercaptans were prepared by the catalytic method of Kramer and Reid.⁶

PROCEDURE.

1. *Preparation of anthraquinone-thio-ether-sulfonic-acids.*

Anthraquinone 1,8 di-sodium-sulfonate was suspended in boiling water containing about two equivalents of caustic soda. In the case of the more volatile mercaptans, methyl and ethyl, the mercaptans were generated in another flask, as previously described and passed, in vapor form, into the alkaline reaction mixture which was gently boiled and vigorously stirred. The less volatile mercaptans were weighed into the alkaline mixture and boiled under reflux. Slightly more than enough mercaptan to replace one sulfonic acid group was used. Since all the 1,8 thio-ether-sulfonic-acids are comparatively soluble the formation of di-thio-ether is favored, so that the reaction must be stopped at the proper time in order to get a minimum amount of the di-thio-ether. This was separated from the dried thio-ether-sulfonic acid by extraction with boiling benzene after which the salt was recrystallized from water.

II. *Preparation of anthraquinone di-thio-ethers.*

When the di-thio-ethers were desired more mercaptan

6 Private communication.

was used and the heating continued until the second sulfonic acid group was replaced.

The mixed di-thio-ethers were obtained by gently boiling an alkaline suspension of the purified anthraquinone thio-ether-sodium sulfonate with a different mercaptan. Owing to the greater solubility of the thio-ether-sodium-sulfonates derived from the relatively lower mercaptans it was found preferable to employ the mercaptan of higher molecular weight last.

The separation of yellow or reddish yellow needles indicated the course of the reaction. The product was filtered, washed with hot water until the filtrate was colorless, dried and re-crystallized from benzene.

III. *Preparation of Sulfones.*

The sulfones were prepared by oxidizing the anthraquinone di-thio-ethers with fuming nitric acid. The reaction product was poured into hot water, filtered and washed.

IV. *Preparation of Salts.*

The metallic and organic salts of the above acids were prepared by adding a solution of nitrate, chloride or sulfate of the desired base to a hot solution of an equivalent amount of the anthraquinone-thio-ether-sodium-sulfonate. The less soluble salt separating out. The nearly insoluble salts were purified by boiling with water.

V. *Analytical*

1. *Sulfur.*

Sulfur was determined by means of the Parr bomb, using 0.2 gram samples and 5.0 grams of sodium peroxide, with subsequent precipitation of barium sulfate.

2. *Water of Hydration.*

1.0 gram samples were exposed to an atmosphere of 50% humidity for 48 hours, then heated to constant weight in a vacuum at 110°C. 2 to 4 hours being generally

sufficient to remove all the water. A dead air humidor containing 44% sulfur acid was used to obtain the 50% humidity. A modified and enlarged Abdenhalden vapor-vacuum oven, capable of holding four 100mm combustion boats was designed and constructed according to the following plan.

3. *Sodium, Barium, Strontium, Calcium, Nickel and Cobalt.*

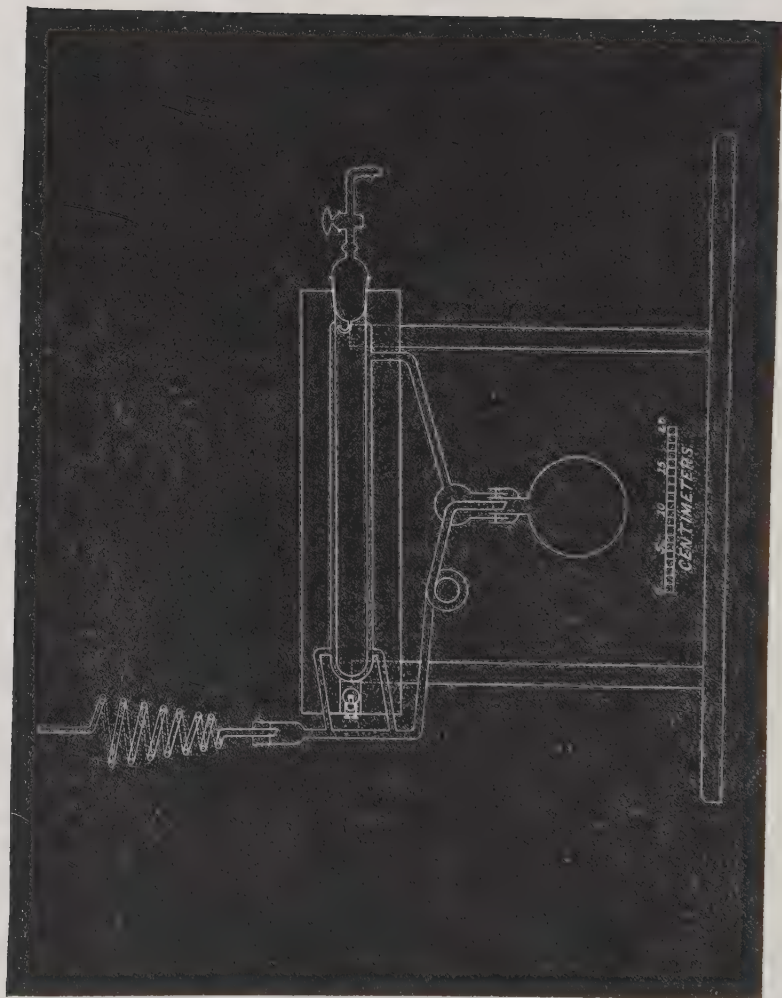
0.5 gram samples, dried as above, were ignited in a platinum crucible until the carbon was burned off as completely as possible. The residue was then evaporated with concentrated sulfuric acid, and re-ignited with ammonium carbonate to constant weight. The metal was weighed as the sulfate.

4. *Lead.*

0.5 gram samples were ignited cautiously, and evaporated with nitric acid to dissolve any reduced lead. The residue was evaporated with concentrated sulfuric acid and re-ignited with ammonium carbonate to constant weight. The metal was weighed as the sulfate.

5. *Copper.*

The copper was precipitated in a faintly ammoniacal solution with hydrogen sulfide. The precipitate was filtered, dried, ignited and weighed as cupric oxide. Inasmuch as the percentage of copper is the same in cupric oxide and cuprous sulfide the combustion was not complete.



ANTHRAQUINONE-1-THIO-ETHER-8-SULFONIC ACIDS.

Anthraquinone-1-Methyl Thio-Ether-8-Sodium-Sulfonate



Methyl mercaptan was passed for two hours into a suspension of 82 grams of anthraquinone 1-8 di-sodium-sulfonate in 25 grams of sodium hydroxide and 500 cc. water. Yield 57 grams of a brick red crystalline powder which does not melt at 300° C.

Substance 1.0061 g. lost 0.0487 g.

Calculated for $\text{C}_{15}\text{H}_9\text{O}_5\text{S}_2\text{Na} \cdot \text{H}_2\text{O}$: H_2O 4.81% found 4.84%.

Substance anhydrous 0.5006 gave 0.1021 g. Na_2SO_4 .

Calculated for $\text{C}_{15}\text{H}_9\text{O}_5\text{S}_2\text{Na}$: Na 6.45% found 6.60%.

Anthraquinone-1-Methyl-Thio-Ether-8-Barium Sulfonate.



Crystallizes from water in dark brick red needles which do not melt at 300°C.

Substance 0.5003 g. gave 0.1422 g. BaSO_4 .

Calculated for $(\text{C}_{15}\text{H}_9\text{O}_5\text{S}_2)_2\text{Ba}:\text{Ba}$. 17.09% found 16.73%.

Aniline Salt of Anthraquinone-1-Methyl Thio-Ether-8-Sulfonic Acid.

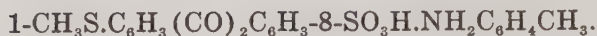


Crystallizes in orange needles which melt at about 260° with decomposition.

Substance 0.2000 g. gave 0.2161 g. BaSO_4 .

Calculated for $\text{C}_{21}\text{H}_{17}\text{O}_5\text{S}_2\text{N}:\text{S}_2$. 15.00% found 14.85%.

Ortho Toluidine Salt of Anthraquinone-1-Methyl-Thio-Ether-8-Sulfonic Acid.



Yellow needles which melt at about 255°C with decomposition.

Substance 0.2007 g. gave 0.2087 g. BaSO_4 .

Calculated for $\text{C}_{22}\text{H}_{19}\text{O}_5\text{S}_2\text{N}:\text{S}_2$. 14.53% found 14.30%.

Para Toluidine Salt of Anthraquinone-1-Methyl-Thio-Ether-8-Sulfonic Acid.



Orange needles which melt at about 260° with decomposition.

Substance 0.2011 g. gave 0.2107 g. BaSO_4 .

Calculated for $\text{C}_{22}\text{H}_{19}\text{O}_5\text{S}_2\text{N}:\text{S}_2$. 14.53% found 14.37%.

Anthraquinone-1-Ethyl-Thio-Ether-8-Sodium Sulfonate.



Gaseous ethyl mercaptan was passed into 82 grams of anthraquinone 1-8 di-sodium sulfonate suspended in 500 cc. of water and 25 grams of sodium hydroxide for 3 hours. Yield 45 grams of orange red needles which do not melt at 300°C.

Substance 0.3031 g. gave 0.0571 g. Na_2SO_4 .

Calculated for $\text{C}_{16}\text{H}_{11}\text{O}_5\text{S}_2\text{Na}:\text{Na}$ 6.21% found 6.11%.

Anthraquinone-1-Ethyl-Thio-Ether-8-Barium Sulfonate.



Orange red needles which do not melt at 300°C.

Substance 0.3009 g. gave 0.0834 g. BaSO_4 .

Calculated for $(\text{C}_{16}\text{H}_{11}\text{O}_5\text{S}_2)_2\text{Ba}:\text{Ba}$. 16.51% found 16.31%.

Anthraquinone-1-Propyl-Thio-Ether-8-Sodium Sulfonate.

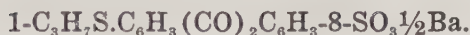
82 grams of anthraquinone 1-8 di-sodium sulfonate, suspended in 500 cc. water and 8 grams sodium hydroxide were refluxed with 40 grams of 80% propyl mercaptan for three hours. Yield 21 grams of ochre yellow crystalline powder which melts at 289°C.

Substance 1.0063 g. lost 0.0228 g.

Calculated for $\text{C}_{17}\text{H}_{13}\text{O}_5\text{S}_2\text{Na}\frac{1}{2}\text{H}_2\text{O}:\frac{1}{2}\text{H}_2\text{O}$. 2.29%
found 2.26%.

Substance 0.5025 g. gave 0.0967 g. Na_2SO_4 .

Calculated for $\text{C}_{17}\text{H}_{13}\text{O}_5\text{S}_2\text{Na}:\text{Na}$. 5.98% found 6.23%.

Anthraquinone-1-Propyl-Thio-Ether-8-Barium Sulfonate.

Orange powder does not melt at 300°C.

Substance 0.3003 g. gave 0.0821 g. BaSO_4 .

Calculated for $(\text{C}_{17}\text{H}_{13}\text{O}_5\text{S}_2)_2\text{Ba}:\text{Ba}$. 15.97% found
16.08%.

Aniline Salt of Anthraquinone-1-Propyl-Thio-Ether-8-Sulfonic Acid.

Orange needles which melt at about 250° with decomposition.

Substance 0.2012 g. gave 0.2054 g. BaSO_4 .

Calculated for $\text{C}_{23}\text{H}_{21}\text{O}_5\text{S}_2\text{N}:\text{S}_2$. 14.08% found 14.01%.

Ortho Toluidine Salt of Anthraquinone-1-Propyl-Thio-Ether-8-Sulfonic Acid.

Yellow needles which melt about 260°C with decomposition.

Substance 0.2016 g. gave 0.2003 g. BaSO_4 .

Calculated for $\text{C}_{24}\text{H}_{23}\text{O}_5\text{S}_2\text{N}:\text{S}_2$. 13.66% found 13.64%.

Para Toluidine Salt of Anthraquinone-1-Propyl-Thio-Ether-8-Sulfonic Acid.



Orange yellow needles which melt at about 255°C with decomposition.

Substance 0.2006 g. gave 0.1983 g. $BaSO_4$.

Calculated for $C_{24}H_{23}O_5S_2N:S_2$. 13.66% found 13.56%.

Anthraquinone-1-Butyl-Thio-Ether-8-Sodium Sulfonate.



82 grams of anthraquinone 1-8 di-sodium sulfonate suspended in 500 cc. of water and 8 grams of sodium hydroxide were refluxed with 30 grams of butyl mercaptan for two hours. Yield 30 grams of orange yellow needles which do not melt at 300°C.

Substance 3.2320 g. lost 0.1420 g.

Calculated for $C_{18}H_{15}O_5S_2Na.H_2O:H_2O$. 4.33% found 4.39%.

Substance 0.5046 g. gave 0.0872 g. Na_2SO_4 .

Calculated for $C_{18}H_{15}O_5S_2Na:Na$ 5.77% found 5.59%.

Anthraquinone-1-Butyl-Thio-Ether-8-Barium Sulfonate.

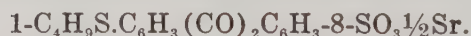


Fine orange yellow needles which do not melt at 300°C.

Substance 0.5008 g. gave 0.1285 g. $BaSO_4$.

Calculated for $(C_{18}H_{15}O_5S_2)_2Ba:Ba$. 15.47% found 15.12%.

Anthraquinone-1-Butyl-Thio-Ether-8-Strontium Sulfonate.



Orange red crystalline powder which does not melt at 300°C.

Substance 0.5007 g. gave 0.1116 g. $Sr.SO_4$.

Calculated for $(C_{18}H_{15}O_5S_2)_2Sr:Sr$. 10.45% found 10.63%.

Anthraquinone-1-Butyl-Thio-Ether-8-Calcium Sulfonate.

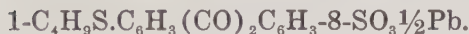
Red crystalline powder which does not melt at 300°C.

Substance 1.0006 g. lost 0.0788 g.

Calculated for $\text{C}_{18}\text{H}_{15}\text{O}_5\text{S}_2\frac{1}{2}\text{Ca.4 H}_2\text{O:4 H}_2\text{O. 8.35\%}$
found 7.87%.

Substance 0.5021 g. gave 0.0871 g. CaSO_4 .

Calculated for $(\text{C}_{18}\text{H}_{15}\text{O}_5\text{S}_2)_2 \text{Ca:Ca. 5.07\%}$ found 5.10%.

Anthraquinone-1-Butyl-Thio-Ether-8-Lead Sulfonate.

Orange red powder which does not melt at 300°C.

Substance 0.5008 g. gave 0.1590 g. PbSO_4 .

Calculated for $(\text{C}_{18}\text{H}_{15}\text{O}_5\text{S}_2)_2 \text{Pb:Pb. 21.63\%}$ found 21.69%.

Anthraquinone-1-Butyl-Thio-Ether-8-Nickel Sulfonate.

Orange red needles which do not melt at 300°C. The water of hydration is undetermined.

Substance 0.5025 g. gave 0.0938 g. NiSO_4 .

Calculated for $(\text{C}_{18}\text{H}_{15}\text{O}_5\text{S}_2)_2\text{Ni:Ni. 7.25\%}$ found 7.08%.

Anthraquinone-1-Butyl-Thio-Ether-8-Cobalt Sulfonate.

Orange red needles which do not melt at 300°C. The water of hydration is undetermined.

Substance 0.5061 g. gave 0.0985 g. CoSO_4 .

Calculated for $(\text{C}_{18}\text{H}_{15}\text{O}_5\text{S}_2)_2 \text{Co:Co. 7.28\%}$ found 7.40%.

Anthraquinone-1-Butyl-Thio-Ether-8-Copper Sulfonate.

Ochre yellow powder which does not melt at 300°C.

Substance 1.0040 g. lost 0.0342 g.

Calculated for $\text{C}_{18}\text{H}_{15}\text{O}_5\text{S}_2\frac{1}{2}\text{Cu.1}\frac{1}{2}\text{H}_2\text{O}:\frac{1}{2}\text{H}_2\text{O}$. 3.21%
found 3.40%.

Substance 0.2000 g. gave 0.0196 g. CuO.

Calculated for $(\text{C}_{18}\text{H}_{15}\text{O}_5\text{S}_2)_2\text{Cu}:\text{Cu}$. 7.81% found
7.85%.

Aniline Salt of Anthraquinone-1-Butyl-Thio-Ether-8-Sulfonic Acid.

Yellow needles which melt at about 242°C with decomposition.

Substance 0.2000 g. gave 0.2014 g. BaSO_4 .

Calculated for $\text{C}_{24}\text{H}_{23}\text{O}_5\text{S}_2\text{N}:\text{S}_2$. 13.66% found 13.85%.

Ortho Toluidine Salt of Anthraquinone-1-Butyl-Thio-Ether-8-Sulfonic Acid.

Yellow needles which melt at about 260°C with decomposition.

Substance 0.2000 g. gave 0.1979 g. BaSO_4 .

Calculated for $\text{C}_{25}\text{H}_{25}\text{O}_5\text{S}_2\text{N}:\text{S}_2$. 13.26% found 13.60%.

Para Toluidine Salt of Anthraquinone-1-Butyl-Thio-Ether-8-Sulfonic Acid.

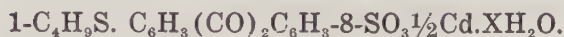
Yellow needles which melt at about 260°C with decomposition.

Substance 0.2000 g. gave 0.1965 g. BaSO_4 .

Calculated for $\text{C}_{25}\text{H}_{25}\text{O}_5\text{S}_2\text{N}:\text{S}_2$. 13.26% found 13.50%.

Anthraquinone-1-Butyl-Thio-Ether-8-Silver Sulfonate.

Canary yellow needles.

Anthraquinone-1-Butyl-Thio-Ether-8-Cadmium Sulfonate.

Orange needles.

Anthraquinone-1-Butyl-Thio-Ether-8-Mercuric Sulfonate.

Orange needles.

Anthraquinone-1-Butyl-Thio-Ether-8-Manganese Sulfonate.

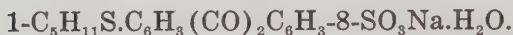
Red needles.

Anthraquinone-1-Butyl-Thio-Ether-8-Zinc Sulfonate.

Orange red needles.

Anthraquinone-1-Butyl-Thio-Ether-8-Aluminium Sulfonate.

Orange red needles.

Anthraquinone-1-Iso-Amyl-Thio-Ether-8-Sodium Sulfonate.

82 grams of anthraquinone 1-8 di-sodium sulfonate suspended in 500 cc. water and 10 grams sodium hydroxide were refluxed with 32 grams of 80% iso-amyl mercaptan for four hours. Yield 50 grams of brownish orange needles which do not melt at 300°C.

Substance 1.0039 g. lost 0.0418 g.

Calculated for $C_{19}H_{17}O_5S_2Na.H_2O:H_2O$. 4.19% found 4.16%.

Substance 0.5011 g. gave 0.0841 g. Na_2SO_4 .

Calculated for $C_{19}H_{17}O_5S_2Na:Na$. 5.58% found 5.34%.

Anthraquinone-1-Iso-Amyl-Thio-Ether-8-Barium Sulfonate.

Orange yellow needles which do not melt at 300°C.

Substance 0.5021 g. gave 0.1262 g. $BaSO_4$.

Calculated for $(C_{19}H_{17}O_5S_2)_2Ba:Ba$. 14.99% found 14.80%.

Aniline Salt of Anthraquinone-1-Iso-Amyl-Thio-Ether-8-Sulfonic Acid.

Orange needles which melt at about 260°C with decomposition.

Substance 0.2004 g. gave 0.1966 g. $BaSO_4$.

Calculated for $C_{25}H_{25}O_5S_2N:S_2$. 13.26% found 13.47%.

Ortho Toluidine Salt of Anthraquinone-1-Iso-Amyl-Thio-Ether-8-Sulfonic Acid.

Orange needles which melt at about 260°C with decomposition.

Substance 0.2005 g. gave 0.1911 g. $BaSO_4$.

Calculated for $C_{26}H_{27}O_5S_2N:S_2$. 12.89% found 13.06%.

Para Toluidine Salt of Anthraquinone-1-Iso-Amyl-Thio-Ether-8-Sulfonic Acid.



Orange needles which melt at about 255°C with decomposition.

Substance 0.2005 g. gave 0.1896 g. BaSO_4 .

Calculated for $\text{C}_{26}\text{H}_{27}\text{O}_5\text{S}_2\text{N}:\text{S}_2$ 12.88% found 12.98%.

ANTHRAQUINONE-1-8-DI-THIO-ETHERS.**Anthraquinone-1-8-Di-Methyl-Thio-Ether.**

This compound was obtained as a by-product in the preparation of anthraquinone 1-methyl-thio-ether-8-sodium sulfonate. It crystallized from benzene in lustrous brownish yellow needles which melt at 222°C.

Substance 0.2000 g. gave 0.3075 g. BaSO_4 .

Calculated for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}_2\text{:S}_2$. 21.35% found 21.11%.

Sulfone.

Yellow white powder which melts at 310°C.

Substance 0.2000 g. gave 0.2527 g. BaSO_4 .

Calculated for $\text{C}_{16}\text{H}_{12}\text{O}_6\text{S}_2\text{:S}_2$. 17.60% found 17.35%

Anthraquinone-1-Methyl-8-Ethyl-Di-Thio-Ether.

Gaseous ethyl mercaptan was passed into a solution of 6 grams of anthraquinone-1-methyl-thio-ether-8-sodium sulfonate in 300 cc. of water and 1 gram of sodium hydroxide for 3 hours. Yield 3.5 grams of red crystals which melt at 210°C.

Substance 0.2009 g. gave 0.2988 g. BaSO_4 .

Calculated for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}_2\text{:S}_2$. 20.40% found 20.45%.

Sulfone.

Pale yellow crystalline powder which melts at 220°C.

Substance 0.2000 g. gave 0.2446 g. BaSO_4 .

Calculated for $\text{C}_{17}\text{H}_{14}\text{O}_6\text{S}_2\text{:S}_2$. 16.95% found 16.79%.

Anthraquinone-1-Methyl-8-Propyl-Di-Thio-Ether.

6 grams of anthraquinone-1-methyl-thio-ether-8-sodium sulfonate dissolved in 300 cc. of water and 1 gram of sodium hydroxide were refluxed with 2 grams of 80% propyl mercaptan for three hours. Yield 5 grams of orange red needles which melt at 173.5°C .

Substance 0.2000 g. gave 0.2854 g. BaSO_4 .

Calculated for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}_2\text{:S}_2$. 19.53% found 19.60%.

Sulfone.

Yellow white powder which melts at 211°C .

Substance 0.2000 g. gave 0.2386 g. BaSO_4 .

Calculated for $\text{C}_{18}\text{H}_{16}\text{O}_6\text{S}_2\text{:S}_2$. 16.34% found 16.38%.

Anthraquinone-1-Methyl-8-Butyl-Di-Thio-Ether.

6 grams of anthraquinone-1-methyl-thio-ether-8-sodium sulfonate dissolved in 250 cc. of water and 1 gram of sodium hydroxide were refluxed with 2 grams of butyl mercaptan for three hours. Yield 4 grams of orange needles which melt at 134°C .

Substance 0.2001 g. gave 0.2731 g. BaSO_4 .

Calculated for $\text{C}_{19}\text{H}_{18}\text{O}_2\text{S}_2\text{:S}_2$. 18.73% found 18.74%.

Sulfone.

Light yellow powder which melts at 169°C .

Substance 0.2022 g. gave 0.2266 g. BaSO_4 .

Calculated for $\text{C}_{19}\text{H}_{18}\text{O}_6\text{S}_2\text{:S}_2$. 15.78% found 15.38%.

Anthraquinone-1-Methyl-8-Iso-Amyl-Di-Thio-Ether.

7 grams of anthraquinone-1-methyl-thio-ether-8-sodium hydroxide were refluxed with 2 grams of 80% iso amyl mercaptan for three hours. Yield 3.5 grams of fine orange needles which melt at 114°C .

Substance 0.2017 g. gave 0.2661 g. BaSO_4 .

Calculated for $\text{C}_{20}\text{H}_{20}\text{O}_2\text{S}_2\text{:S}_2$, 17.99% found 18.10%.

Sulfone.

Brown powder which melts at 172°C .

Substance 0.2009 g. gave 0.2208 g. BaSO_4 .

Calculated for $\text{C}_{20}\text{H}_{20}\text{O}_6\text{S}_2\text{:S}_2$, 15.25% found 15.09%.

Anthraquinone 1-8-Di-Ethyl-Thio-Ether.

This compound was obtained as a by-product in the preparation of anthraquinone-1-ethyl-thio-ether-8-sodium sulfonate. It crystallizes from benzene in red crystals which melt at 167.5°C .

Substance 0.2006 g. gave 0.2842 g. BaSO_4 .

Calculated for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}_2\text{:S}_2$, 19.53% found 19.44%.

Sulfone.

Pale yellow crystalline powder which melts at 228°C .

Substance 0.2000 g. gave 0.2368 g. BaSO_4 .

Calculated for $\text{C}_{18}\text{H}_{16}\text{O}_6\text{S}_2\text{:S}_2$, 16.35% found 16.26%.

Anthraquinone-1-Ethyl-8-Butyl-Di-Thio-Ether.

10 grams of anthraquinone-1-butyl-thio-ether-8-sodium sulfonate suspended in 50 cc. of water and 1 gram sodium hydroxide were refluxed with 5 grams ethyl mercaptan for three hours. Yield three grams of orange yellow needles which melt at 95°C .

Substance 0.2007 g. gave 0.2664 g. BaSO_4 .

Calculated for $\text{C}_{20}\text{H}_{20}\text{O}_2\text{S}_2:\text{S}_2$. 17.99% found 18.14%.

Sulfone.

Yellow white crystalline powder which melts at 128°C .

Substance 0.2000 g. gave 0.2249 g. BaSO_4 .

Calculated for $\text{C}_{20}\text{H}_{20}\text{O}_6\text{S}_2:\text{S}_2$. 15.25% found 15.45%.

Anthraquinone-1-8-Di-Propyl-Thio-Ether.

This compound was obtained as a by-product from the preparation of anthraquinone 1-propyl-thio-ether-8-sodium sulfonate. It crystallizes from benzene in brick red prisms which melts at 142°C .

Substance 0.2003 g. gave 0.2609 g. BaSO_4 .

Calculated for $\text{C}_{20}\text{H}_{20}\text{O}_2\text{S}_2:\text{S}_2$. 17.99% found 17.87%.

Sulfone.

Yellow white crystalline powder which melts at 210°C .

Substance 0.2007 g. gave 0.2159 g. BaSO_4 .

Calculated for $\text{C}_{20}\text{H}_{20}\text{O}_6\text{S}_2:\text{S}_2$. 15.25% found 14.80%.

Anthraquinone-1-Propyl-8-Butyl-Di-Thio-Ether.

5 grams of anthraquinone 1-butyl-thio-ether-8-sodium sulfonate suspended in 50 cc. of water and 1 gram of sodium hydroxide were refluxed with 2.5 grams of 80% propyl mercaptan for six hours. Yield 5 grams of orange needles which melted at 119.5°C.

Substance 0.2000 g. gave 0.2507 g. BaSO₄.

Calculated for C₂₁H₂₂O₂S₂:S₂, 17.31% found 17.20%.

Sulfone.

Yellow white crystalline powder which melts at 200.5°C.

Substance 0.2000 g. gave 0.2142 g. BaSO₄.

Calculated for C₂₁H₂₂O₆S₂:S₂, 14.76% found 14.70%.

Anthraquinone-1-Propyl-8-Iso-Amyl-Di-Thio-Ether.

7 grams of anthraquinone 1-propyl-thio-ether-8-sodium sulfonate dissolved in 250 cc. of water and 1 gram sodium hydroxide were refluxed with 2.5 grams of 80% iso-amyl mercaptan for four hours. Yield 4 grams of orange powder which melts at 104°C.

Substance 0.2027 g. gave 0.2444 g. BaSO₄.

Calculated for C₂₂H₂₄O₂S₂:S₂ 16.68% found 16.58%.

Sulfone.

Brown powder melting at 147.5°C.

Substance 0.2000 g. gave 0.2034 g. BaSO₄.

Calculated for C₂₂H₂₄O₆S₂:S₂ 14.30% found 13.95%.

Anthraquinone-1-8-Di-Butyl-Thio-Ether.

This compound was obtained as a by-product in the preparation of anthraquinone 1-butyl-thio-ether-8-sodium sulfonate. It crystallizes from benzene in orange red needles which melt at 125°C.

Substance 0.2008 g. gave 0.2382 g. BaSO₄.

Calculated for C₂₂H₂₄O₂S₂:S₂ 16.68% found 16.28%.

Sulfone.

Pale yellow crystalline powder which melts at 138°C.

Substance 0.2000 g. gave 0.2040 g. BaSO₄.

Calculated for C₂₂H₂₄O₆S₂:S₂ 14.30% found 14.00%.

Anthraquinone-1-Butyl-8-Iso-Butyl-Di-Thio-Ether.

7 grams of anthraquinone 1-butyl-thio-ether-8-sodium sulfonate dissolved in 250 cc. of water and 1 gram of sodium hydroxide were refluxed with 2.5 grams of iso butyl mercaptan for 3 hours. Yield 4 grams of orange colored prisms which melt at 103.5°C.

Substance 0.2000 g. gave 0.2429 g. BaSO₄.

Calculated for C₂₂H₂₄O₂S₂:S₂ 16.68% found 16.70%.

Sulfone.

Light yellow crystalline powder which melts at 168.5°C.

Substance 0.2000 g. gave 0.2034 g. BaSO₄.

Calculated for C₂₂H₂₄O₆S₂:S₂ 14.30% found 13.95%.

Anthraquinone-1-Butyl-8-Iso-Amyl-Di-Thio-Ether.

7 grams of anthraquinone-1-butyl-thio-ether-8-sodium sulfonate dissolved in 300 cc. of water and 1 gram of sodium hydroxide were refluxed with 2 grams of iso-amyl mercaptan for three hours. Yield 4 grams of orange crystals which melt at 116.5°C.

Substance 0.2004 g. gave 0.2366 g. BaSO₄.

Calculated for C₂₃H₂₆O₂S₂:S₂ 16.09% found 16.21%.

Sulfone.

Pale yellow powder which melts at 154°C.

Substance 0.2023 g. gave 0.2055 g. BaSO₄.

Calculated for C₂₃H₂₆O₆S₂:S₂ 13.87% found 13.94%.

Anthraquinone-1-8-Di-Iso-Amyl-Thio-Ether.

This compound was obtained as a by-product in the preparation of anthraquinone 1-iso-amyl-thio-ether-8-sodium sulfonate. It crystallizes from benzene in orange red elongated plates which melt at 133°C.

Substance 0.2004 g. gave 0.2226 g. BaSO₄.

Calculated for C₂₄H₂₈O₂S₂:S₂ 15.55% found 15.27%.

Sulfone.

Yellow needles which melt at 176°C.

Substance 0.2000 g. gave 0.1952 g. BaSO₄.

Calculated for C₂₄H₂₈O₆S₂:S₂ 13.46% found 13.40%.

BIOGRAPHY.

George Edgar Miller was born in Abbottstown, Pennsylvania, November 13, 1891. His early education was received in the public schools of that place. In 1905 he removed to Gettysburg where he finished his grammar school work and was graduated from High School in 1910. The same year he entered Gettysburg College and was awarded the degree of Bachelor of Science in 1914. The years 1914-1916 were spent at the University of Pennsylvania in graduate work in Chemistry. The next year, 1916-17 he attended the Johns Hopkins University taking Chemistry as his major, and Physical Chemistry and Mineralogy as his minor subjects. The next two years he spent with E. I. du Pont de Nemours & Company at Wilmington, Delaware. The year 1919-20 he was again in attendance, in the graduate chemistry department, of the Johns Hopkins University.

